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FINAL REPORT

ON

CONTRACT WITH CANMET

Serial No. OST84-00418

1. Spectrum fits

All spectrum fits have now been submitted to Dr. L.J. Cabri.

2. Auxiliary computing

All auxiliary calculations have been done and the results submitted to Dr. Cabri.

3. General conclusions on the measurements and analysis

A subsidiary report on various issues that arose during the analysis is attached. It indicates possible improvements to the experimental techniques used to generate the data submitted to us for analysis.

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3 pp

SUBSIDIARY CONCLUSIONS ON 1985 CANMET PIXE ANALYSIS

1. Quality of least-squares fits (Heidelberg)

The Heidelberg sphalerite results show a worsening of χ_r^2 as the Cd K X-ray intensity grows. Variation of the Si(Li) detector thickness and aluminum filter thickness have little effect on this, hence the effect does not arise from inaccurate knowledge of these parameters. Nor is the effect a result of exclusion of Cd (nominally a trace element) from the matrix (ZnS) used by the code; variation of the Cd contribution to the matrix (from 0-2%) has no effect on χ^2, and negligible effect on the Kβ/Kα ratios of both Zn and Cd.

However if instead of fitting the channel region 100-1024, we performed two separate fits to regions 100-600 and 600-1024, the fits improved greatly. For example in a case where $\chi_r^2 = 8.24$ for the whole spectrum, the 100-600 region (dominated by Zn) gave $\chi_r^2 = 1.55$, and the upper (Cd) region gave $\chi_r^2 = 1.33$.

We conclude that the electronic system used at Heidelberg is slightly non-linear. Due to the manner in which we use standards, the effects of this on concentrations derived from full-spectrum fits are only at the 1-2% level. It would be too time-consuming to double the number of fits, and it would often be difficult to split up highly populated spectra. Hence an attempt to improve the electronics at Heidelberg is indicated.

2. Fit quality (LASL)

The LASL χ_r^2 values are similar (1-10) to the Heidelberg values. However the spectral intensities in the matrix peaks (Fe, Zn) are nearly an order of magnitude greater at LASL. Since χ_r^2 inflates linearly with intensity, one would have expected the LASL fits to give much larger χ_r^2 values. The fact that they do not suggests that there is less non-linearity problem at LASL.

3. Matrix K X-rays - Chemical effects

When the LASL sphalerite spectra are split in two fitting regions there is an evident misfit in the high-statistics Zn K X-ray region. The Kβ/Kα intensity ratio appears to be higher than we expect from the precisely known theoretical ratio corrected for filter attenuation. Addition of radiative Auger satellites does not improve the situation. We attribute the effect to the chemical bonding of the Zn atom.

An experimental study of this effect, using synthetic sulfide specimens made at CANMET, has been launched, under NSERC funding. It's results should help us improve our fitting code (no existing code allows for chemical effects) for use in future CANMET analyses.

4. Surface contamination

As a byproduct of this work, new codes have been written to generate the equivalent surface thickness that would give the same X-ray intensity as would a homogeneous distribution of a given trace element. This code proved to be useful in assessing whether surface lead contamination could affect the accuracy of particular LASL data.

5. Standardization

The calibration technique used at Heidelberg is satisfactory. However we recommend that the Pd and Se trace elements in pyrrotite standards be extended by including Cu. This will improve accuracy for trace elements having $Z \sim 30$.

The lack of calibration hardware at LASL forced us to derive properties of that system from standard spectra. The ad hoc approach that we invented appeared to work reasonably well, but it is not to be regarded as a substitute for proper calibration using proton intensity measurements.

A manuscript comparing the two standardization methods is in preparation.